

2.0 The K_d Model

The simplest and most common method of estimating contaminant retardation is based on the partition (or distribution) coefficient, K_d . The K_d parameter is a factor related to the partitioning of a contaminant between the solid and aqueous phases. It is an empirical unit of measurement that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. The K_d metric is the most common measure used in transport codes to describe the extent to which contaminants are sorbed to soils. It is the simplest, yet least robust model available. A primary advantage of the K_d model is that it is easily inserted into hydrologic transport codes to quantify reduction in the rate of transport of the contaminant relative to groundwater, either by advection or diffusion. Technical issues, complexities, and shortcomings of the K_d approach to describing contaminant sorption to soils are summarized in detail in Chapter 2 of Volume I. Particular attention is directed at issues relevant to the selection of K_d values from the literature for use in transport codes.

The partition coefficient, K_d , is defined as the ratio of the quantity of the adsorbate adsorbed per mass of solid to the amount of the adsorbate remaining in solution at equilibrium. For the reaction



the mass action expression for K_d is

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i} \quad (2.1)$$

where A = free or unoccupied surface adsorption sites

C_i = total dissolved adsorbate remaining in solution at equilibrium

A_i = amount of adsorbate on the solid at equilibrium.

The K_d is typically given in units of ml/g. Describing the K_d in terms of this simple reaction assumes that A is in great excess with respect to C_i and that the activity of A_i is equal to 1.

Chemical retardation, R_f , is defined as,

$$R_f = v_p/v_c \quad (2.2)$$

where v_p = velocity of the water through a control volume

v_c = velocity of contaminant through a control volume.

The chemical retardation term does not equal unity when the solute interacts with the soil; almost always the retardation term is greater than 1 due to solute sorption to soils. In rare cases, the retardation factor

is actually less than 1, and such circumstances are thought to be caused by anion exclusion (See Volume I, Section 2.8). Knowledge of the K_d and of media bulk density and porosity for porous flow, or of media fracture surface area, fracture opening width, and matrix diffusion attributes for fracture flow, allows calculation of the retardation factor. For porous flow with saturated moisture conditions, the R_f is defined as

$$R_f = 1 + (p_b/n_e)K_d \quad (2.3)$$

where p_b = porous media bulk density (mass/length³)
 n_e = effective porosity of the media at saturation.

The K_d parameter is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (*e.g.*, adsorbate concentration, solution/electrolyte matrix) in which it was measured. Site-specific K_d values should be used for site-specific contaminant and risk assessment calculations. Ideally, site-specific K_d values should be measured for the range of aqueous and geological conditions in the system to be modeled. However, literature-derived K_d values are commonly used for screening calculations. Suitable selection and use of literature-derived K_d values for use in screening calculations of contaminant transport is not a trivial matter. Among the assumptions implicit with the K_d construct is: (1) only trace amounts of contaminants exist in the aqueous and solid phases, (2) the relationship between the amount of contaminant in the solid and liquid phases is linear, (3) equilibrium conditions exist, (4) equally rapid adsorption and desorption kinetics exists, (5) it describes contaminant partitioning between 1 sorbate (contaminant) and 1 sorbent (soil), and (6) all adsorption sites are accessible and have equal strength. The last point is especially limiting for groundwater contaminant models because it requires that K_d values should be used only to predict transport in systems chemically identical to those used in the laboratory measurement of the K_d . Variation in either the soil or aqueous chemistry of a system can result in extremely large differences in K_d values.

A more robust approach than using a single K_d to describe the partitioning of contaminants between the aqueous and solid phases is the parametric- K_d model. This model varies the K_d value according to the chemistry and mineralogy of the system at the node being modeled. The parametric- K_d value, unlike the constant- K_d value, is not limited to a single set of environmental conditions. Instead, it describes the sorption of a contaminant in the range of environmental conditions used to create the parametric- K_d equations. These types of statistical relationships are devoid of causality and therefore provide no information on the mechanism by which the radionuclide partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. Understanding these mechanisms is extremely important relative to estimating the mobility of a contaminant.

When the parametric- K_d model is used in the transport equation, the code must also keep track of the current value of the independent variables at each point in space and time to continually update the concentration of the independent variables affecting the K_d value. Thus, the code must track many more parameters and some numerical solving techniques (such as closed-form analytical solutions) can

no longer be used to perform the integration necessary to solve for the K_d value and/or retardation factor, R_F . Generally, computer codes that can accommodate the parametric- K_d model use a chemical subroutine to update the K_d value used to determine the R_F , when called by the main transport code. The added complexity in solving the transport equation with the parametric- K_d sorption model and its empirical nature may be the reasons this approach has been used sparingly.

Mechanistic models explicitly accommodate for the dependency of K_d values on contaminant concentration, charge, competing ion concentration, variable surface charge on the soil, and solution species distribution. Incorporating mechanistic adsorption concepts into transport models is desirable because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, truly mechanistic adsorption models are rarely, if ever, applied to complex natural soils. The primary reason for this is because natural mineral surfaces are very irregular and difficult to characterize. These surfaces consist of many different microcrystalline structures that exhibit quite different chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface.

Less attention will be directed to mechanistic models because they are not extensively incorporated into the majority of EPA, DOE, and NRC modeling methodologies. The complexity of installing these mechanistic adsorption models into existing transport codes is formidable. Additionally, these models also require a more extensive database collection effort than will likely be available to the majority of EPA, DOE, and NRC contaminant transport modelers. A brief description of the state of the science is presented in Volume I primarily to provide a paradigm for sorption processes.